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Analysis, construction, characterization, and application of copper nanowires loaded on activated carbon for removal of bromophenol blue in water samples

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ABSTRACT

In the present work, a copper nanowire loaded on activated carbon (Cu-NW-AC) was fabricated and applied as an effective adsorbent for the removal of bromophenol blue (BPB) dye from aqueous solutions and then the percentage of removal was evaluated by UV–Vis spectrophotometer. The synthesized adsorbent was characterized and identified using techniques like Transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET). The effective parameters of the removal process were investigated and optimized by experimental design methodology (EDM) based on response surface methodology (RSM) as a powerful optimization method. EDM is a unique method for following the effects of different factors on the removal process simultaneously. Analysis of variance (ANOVA) was used based on p-values and F-tests to investigate the accuracy and reliability of the used method. The optimized parameters were obtained as BPB concentration of 15 mg L^{-1}, ultrasonic irradiation time of 14 min, adsorbent dosage of 0.018 g and pH= 5.5 under the desirability function. To evaluate the adsorption mechanism and calculation of maximum adsorption capacity, different adsorption isotherms were studied and according to the results, the Langmuir isotherm model showed the highest compatibility due to its higher R^2 (0.9905). Also, the proposed adsorbent represented good adsorption capacity (123.45 mg g^{-1}). Moreover, kinetic studies proved the applicability of the pseudo-second-order model (R^2=0.993) compared to other models. The achieved results confirmed the applicability of Cu-NW-AC as a versatile adsorbent for the removal of dye molecules from aqueous solutions using the adsorption method as a simple, easy, available and versatile method.

1. Introduction

Despite the broad applications of dye molecules in different areas and industries like plastic, textile, cosmetics, paper, and so on, the entrance of these materials into the environment, particularly water sources, has become a global concern [1]. Some of the dye molecules are hazardous and toxic for humans and animals and can cause irrecoverable and progressed diseases like cancer, mutation, and skin problems[2]. Some dye molecules have restricted and complex structures and are stable at high temperatures. So, they can remain in the environment for a long time and introduce some main problems[3]. Amongst different dye molecules, bromophenol

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blue (BPB) is considered an anionic dye that has been extensively applied in different fields such as additives, foods, textiles, and papers [4]. Although it is beneficial, it also can cause main environmental problems and hazardous diseases like carcinogenic activities[5]. These adverse effects of BPB have been exciting for researchers and scientists to deal with and design and use appropriate methods for its removal and treatment from the environment, especially water sources. One of the popular methods for the removal of dye molecules is the adsorption process (AP)[6]. AP is not only easy, cheap, available, and efficient but also can be used at large and industrial scales[7]. These exclusive attributes of AP make it a prevalent method for the removal of different pollutants. AP is based on the application of diverse materials as adsorbents, which can adsorb target analytes (dye molecules, organic molecules, etc…) via different adsorption mechanisms[8]. The proposed adsorbents for dye removal should have some main properties in terms of high chemical, physical, and thermal stability, large number of interaction sites, high adsorption capacity, suitable reusability, and fast adsorption rate[9, 10]. To date, various materials have been used as adsorbents. Activated carbon (AC), as one of the famous and applicable adsorbents, has been extensively used for the removal of dye molecules. This fact is due to exceptional properties of AC like simple and easy preparation, cost-effectiveness, sound surface area, and good adsorption capacity [11, 12]. To improve the adsorption capacity and the removal performance of AC, preparing its composites can be an ideal method. The goal of the presented work was the synthesis, characterization, and utilization of AC as an effective adsorbent for the removal of dyes from aqueous solutions. One of the innovations of this work has been the production of AC using disposable cellulose materials, and this has led to the production of a cheap absorbent. The sponginess of the produced AC also helps to absorb organic chemicals in its pores. Nano-based adsorbents (NBAs) have attracted much attention in recent years. NBAs have the features of a versatile adsorbent like high stability, high surface area, high adsorption capacity, and, most importantly, the ability for modification and production of composition materials [13, 14]. Among different NBAs, NWs are very interesting due to their unique properties like high surface area, high adsorption capacity, and electrical features [15]. Cu-NWs have been broadly used in different fields because they have the properties of suitable adsorbent. A combination of AC and NADS like NW, can produce new types of adsorbents that have unique features, like high stability, high surface area, and high adsorption capacity. Investigation and optimization of the influential factors in the removal process is a vital concept. To this end, different affords have been used till now to use an appropriate approach. One-factor at a time (OFAT) is a traditional optimization approach in which the effect of one factor is followed while the other factors are fixed [16, 17]. In spite that OFAT is simple and easy, it needs to use a high volume of solvents and reagents, and it is also time-consuming. Most importantly, OFAT is not able to evaluate the effects of different parameters simultaneously and is not able to predict valid optimum values. To address these critical disadvantages, experimental design methodology based response surface methodology (RSM) is considered a powerful method and has been extensively applied in removal processes. EDM not only can address the drawbacks of OFAT but also can assess the interactions of effective factors concurrently.

The aim of this study was the synthesis, characterization, and application of Cu-NW-AC as an efficient adsorbent for the removal of BPB from aqueous solutions. Moreover, to investigate the mechanism of interactions and adsorption rate, different isotherm and kinetic models were used and assessed at obtained optimum conditions. The fabricated Cu-NW-AC showed a high capacity for the removal of

BPB, which made it an excellent candidate for the removal of other pollutants, especially dye molecules.

2. Experimental

2.1. Reagents and Instruments

In this study, all materials and reagents like BPB dye, acetone, distillation water, HCl, and NaOH were prepared at their highest purity form from Merck Company (Darmstadt, Germany). All instruments and laboratory equipment, including pH measurement (BP3001 model, Singapore), UV–Vis spectrophotometer (Perkin Elmer Lambda 25, USA), an ultrasonic bath with heating system (XUBA3 model, England), centrifuge system (Germany), and laboratory balance (XB22OA Precisa model, Switzerland) were prepared and used for calculation of removal percentage and adsorption capacity. For characterization and identification of prepared adsorbent, different techniques like TEM (Hitachi H-800 at 200 kV, Japan), and BET (Microtrac Bel Corp, USA) were used.

2.2. Fabrication of Cu-NW-AC

To synthesize Cu-NW, 150 mL of NaOH solution (7.0 molL^{-1}) and 7.5 mL of $Cu(NO_3)_2$ solution (0.1 molL^{-1}) were added to a 250 mL flask. Then, 1.95 mL ethylene diamine 95% and 0.75 mL hydrazine (N_2H_4) solution were added to the flask, respectively. Then, the obtained solution was heated at 60 °C for 45 min in an ultrasonic bath. After 36 min, the color of the solution was changed from blue to bronze. This color change confirmed the formation of Cu-NW. For the preparation of AC, at first, 10 g waste newspaper (as cellulosic source) was fragmented into 5 mm pieces and then dispersed in KOH solution at 80 °C for two h. The (W/W) ratio of newspaper, salt, and distillation water was selected as 1:3:4. Then, the obtained mixture was placed in an oven at 80 °C for 48 h to dry newspaper pieces. In the next step, the proposed newspaper pieces were crushed by mortar and transferred to an open container. The target container was then placed in an oven for two hours at 500 °C. After cooling, the obtained ashes were washed with distillation water for neutralization (to get pH=7.5). In the final step, the achieved ACs were dried for 24 h at 120 ^{0}C and used for further steps. To prepare Cu-NW-AC, 150 mL of prepared Cu-NW solution was added to 30 g of AC in a 250 mL flask and stirred using a magnetic stirrer for four h. The obtained Cu-NW-AC was filtered, washed with water, and then dried at 110 °C for 12 h.

2.3. Preparation of BPB standard solutions

In the preparation of the BPB stock solution, at first, 0.005 g of BPB dye was added to a 100 mL flask and then 100 mL of distillation water was added to the flask (50 mg L^{-1}). For preparation of other solutions, the stock solution was diluted appropriately and then used for further experiments.

2.4. Adsorption experiments

The ultrasonic-assisted adsorption of BPB by Cu-NW-AC was carried out as follows: 15 mg L^{-1} of BPB solution was prepared from the stock solution and then adjusted at pH 5.5. In the next step,0.018 g of adsorbent was added to the BPB solution and sonicated for 14 min. Then, the solution was centrifuged to separate the adsorbent from the dye solution. In the final step, the remaining concentration of BPB was determined by UV–Vis spectrophotometer and removal percentage and adsorption capacity were calculated by the following Equations I and II.

$$R\%=C_0-C_e/C_0*100 \quad \text{(Eq. 1)}$$

$$Q_e=((C_0-C_e)V)/m \quad \text{(Eq.2)}$$

Where C_0 is the initial BPB concentration (mg L^{-1}), C_e is the equilibrium BPB concentration (mg L^{-1}), V is the volume of BPB solution (L), and m is the mass of adsorbent (g). The steps of adsorption and measurement of BPB are shown schematically in Figure 1.

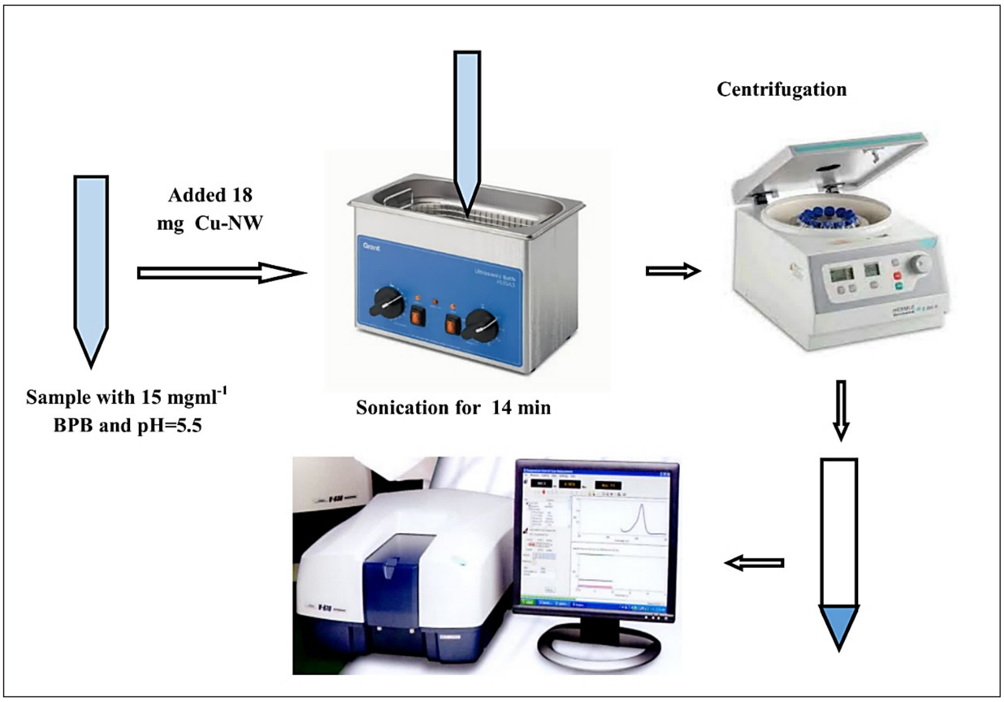

Fig. 1. The steps of adsorption and measurement of BPB

3. Results and discussion

3.1. Characterization of adsorbent

The characterization of the proposed adsorbent, TEM and SEM analyses were used. Using TEM analysis, the morphology and size of the prepared adsorbent can be investigated. According to TEM images (Figure 2A), there are some black areas with high density, which are related to Cu-NW that were distributed on white areas (AC) with low density. According to SEM images of the AC (Figure 2B), it had a porous structure in which the pores had a spherical shape. Moreover, to evaluate the specific surface area and type of adsorbent, BET analysis is proper. So, based on the BET analysis, the fabricated adsorbent had a surface area of 200 g m^{-2}.

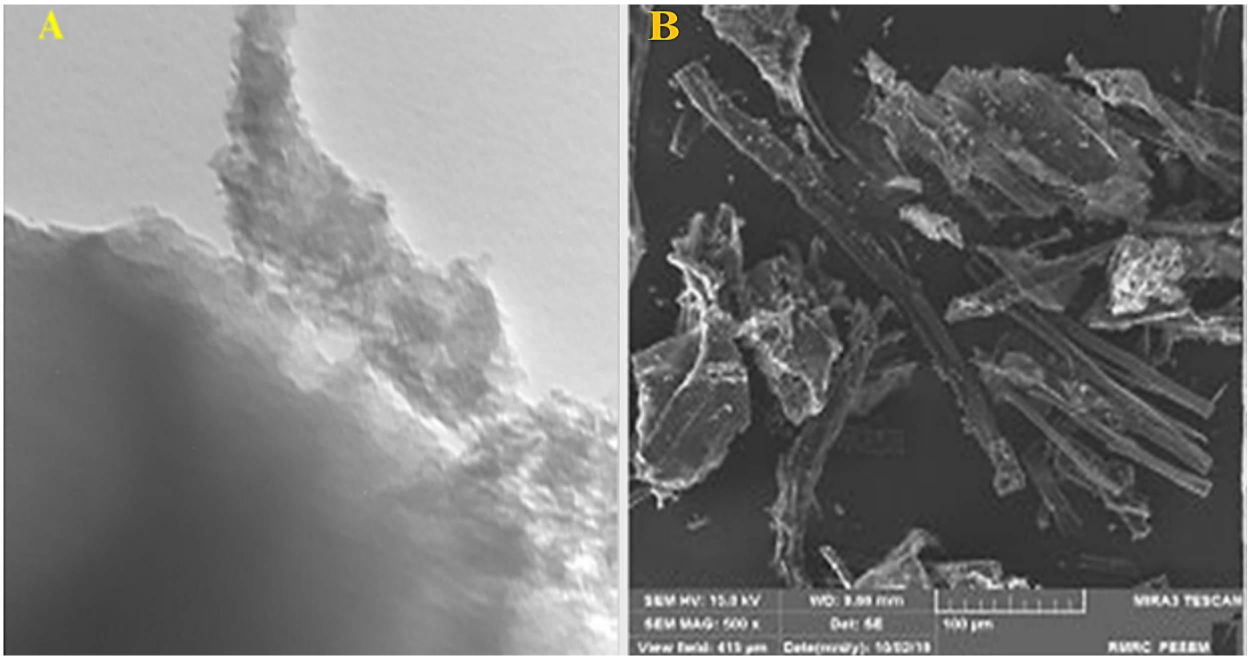

Fig. 2. A) TEM of the Cu-NW-AC B) SEM images of the Cu-NW-AC

3.2. Experimental design methodology based on response surface methodology

In this work, to investigate the influential factors, and their interactions and achieve valid optimum values, RSM was applied. The effects of different variables such as BPB concentration (X_1) (10-30 mgL^{-1}), pH (X_2) (2-10), adsorbent dosage (X_3) (4-20 mg), and sonication time (X_4) (4-16 min) on removal efficiency were optimized using 4 factors at 5 level CCD. The design matrix and the responses for the BPB dye removal using Cu-NW-AC adsorbent are shown in Table 1.

In addition, the accuracy and reliability of the applied method were investigated by ANOVA at a certain confidence level (α = 0.05)(Table 2)[18].To assess the adequacy and reliability of the proposed model, different parameters such as R^2, adjusted R^2, F test, and lack-of-fit test were used. According to the ANOVA analysis, the factors that had p-values less than 0.05 and higher F-values were significant and had significant contributions to the removal process. On the other hand, the parameters with p-values more than 0.05 and lower F-values were not significant and didn't have significant contributions to the removal process[19]. The higher values of R^2 and Adj R^2 proved the accuracy of the used model. Moreover, the lack of a value of more than 0.05 (0.143769) proved the precision and dependability of the recommended model.

Table 1. The design matrix and the responses for the BPB dye removal using Cu-NW-AC adsorbent

Factors	Levels			Star point α=2	
	Low (−1)	Central(0)	High(+1)	-α	+α
(X_1) BPB concentration (mg L^{-1})	15	20	25	10	30
(X_2) pH value	4	6	8	2	10
(X_3) Adsorbent dosage (mg)	8	12	16	4	20
(X_4) Sonication time (min)	7	10	13	4	16

Run	(X_1)	(X_2)	(X_3)	(X_4)	Response (BPB ER%)
1	15	4	8	7	37.47
2	15	4	8	13	52.07
3	15	4	16	7	61.13
4	15	4	16	13	76.79
5	15	8	8	7	39.13
6	15	8	8	13	50.26
7	15	8	16	7	59.86
8	15	8	16	13	79.76
9	25	4	8	7	31.23
10	25	4	8	13	35.88
11	25	4	16	7	34.84
12	25	4	16	13	44.84
13	25	8	8	7	23.40
14	25	8	8	13	30.33
15	25	8	16	7	22.01
16	25	8	16	13	37.79
17	10	6	12	10	78.92
18	30	6	12	10	25.59
19	20	2	12	10	51.17
20	20	10	12	10	31.65
21	20	6	4	10	22.81
22	20	6	20	10	58.97
23	20	6	12	4	25.94
24	20	6	12	16	60.83
25 (C)	20	6	12	10	56.37
26 (C)	20	6	12	10	55.46

(C): Center point
R^2= 0.984
Adj R^2 = 0.965

Table 2. Analysis of variance (ANOVA) for removal of BPB dye using Cu-NW-AC adsorbent.

Source of variation	Sum of square	Df[a]	Mean square	F-value[b]	P value
X_1	3820.579	1	3820.579	9227.337	0.006627
X_2	208.565	1	208.565	503.720	0.028346
X_3	1497.366	1	1497.366	3616.389	0.010585
X_4	1182.028	1	1182.028	2854.795	0.011914
X_1^2	12.988	1	12.988	31.367	0.112483
X_2^2	222.937	1	222.937	538.430	0.027419
X_3^2	239.451	1	239.451	578.314	0.026457
X_4^2	165.592	1	165.592	399.932	0.031807
$X_1 X_2$	75.734	1	75.734	182.909	0.046986
$X_1 X_3$	399.700	1	399.700	965.342	0.020483
$X_1 X_4$	35.790	1	35.790	86.440	0.068211
$X_2 X_3$	1.351	1	1.351	3.264	0.321838
$X_2 X_4$	4.873	1	4.873	11.769	0.180566
$X_3 X_4$	36.090	1	36.090	87.164	0.067930
Lack of Fit	119.795	10	11.980	28.933	0.143769
Pure Error	0.414	1	0.414		
Total SS	10965.01	25			

[a]Df: Degrees of freedom

[b] Test for comparing model variance with residual (error) variance

The relationship between influential factors and response (R%BPB) is presented in Equation 3. Equation 3 confirmed that the effective factors with positive signs had a direct effect on the removal percentage and can increase it. In contrast, the factors with negative signs had the opposite effect and could reduce the removal percentage[20, 21].

$$RE\%=55.915-12.617X_1-2.948X_2+7.899X_3+7.018X_4-3.574X_2^2-3.704X_3^2-3.080X_4^2-2.176X_1X_2-4.998X_1X_3 \quad \text{(Eq.3)}$$

3.3. Response surface methodology for investigating effective variables

RSM uses 3-dimensional (3D) response surface plots to investigate the effects of different factors on the removal process (Figure 3) [22]. According to these plots, increasing BPB concentration can reduce the removal percentage. At low BPB concentrations, the target adsorbent can interact with more dye molecules and remove them. Increasing adsorbent dosage enhanced the removal percentage[23]. In this manner, the functional groups, the specific surface area, and the large reactive surface center of the adsorbent are high and more available to interact with molecule dyes. So, decreasing the adsorbent dosage can decrease the removal percentage. The maximum removal was obtained at a lower pH. BPB is an anionic dye. On the other hand, at higher pH values, since the concentration of hydroxide (OH) is high, the adsorbent can get a negative charge that can produce a repulsive force between the adsorbent and dye molecules and subsequently reduce the removal percentage. As can be seen from 3D plots, enhancing ultrasonic time increased the removal percentage. With increasing time, the possible interactions between adsorbent and dye molecules are increased, which subsequently can raise the removal percentage. After investigating the effective factors, the optimum values were achieved under the desirability function (DF). DF can convert the predicted and experimental response of each factor into a desirability score, while its values between 0.0 and 1.0 show the completely undesirable and fully desired response, respectively. According to the desirability score, maximum recovery (87.455%) was achieved with a BPB concentration of 15 mg L^{-1}, ultrasonic irradiation time (14 min), adsorbent dosage (0.018 g), and pH= 5.5 (Figure 4).

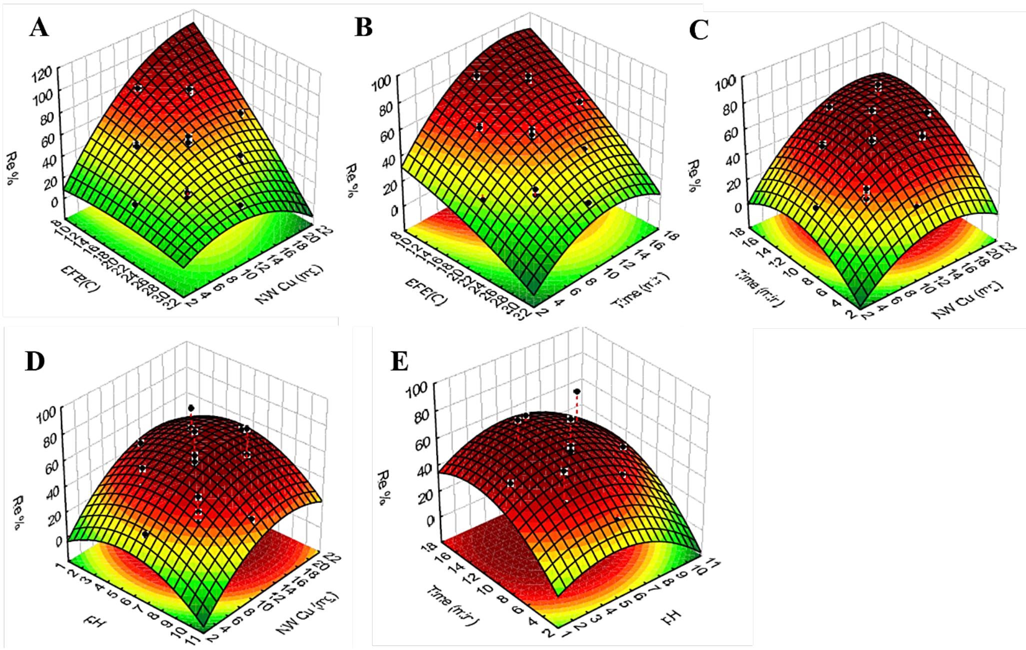

Fig. 3. 3D response surface plots for investigation of the effects of different factors on removal of BPB dye removal using Cu-NW-AC adsorbent

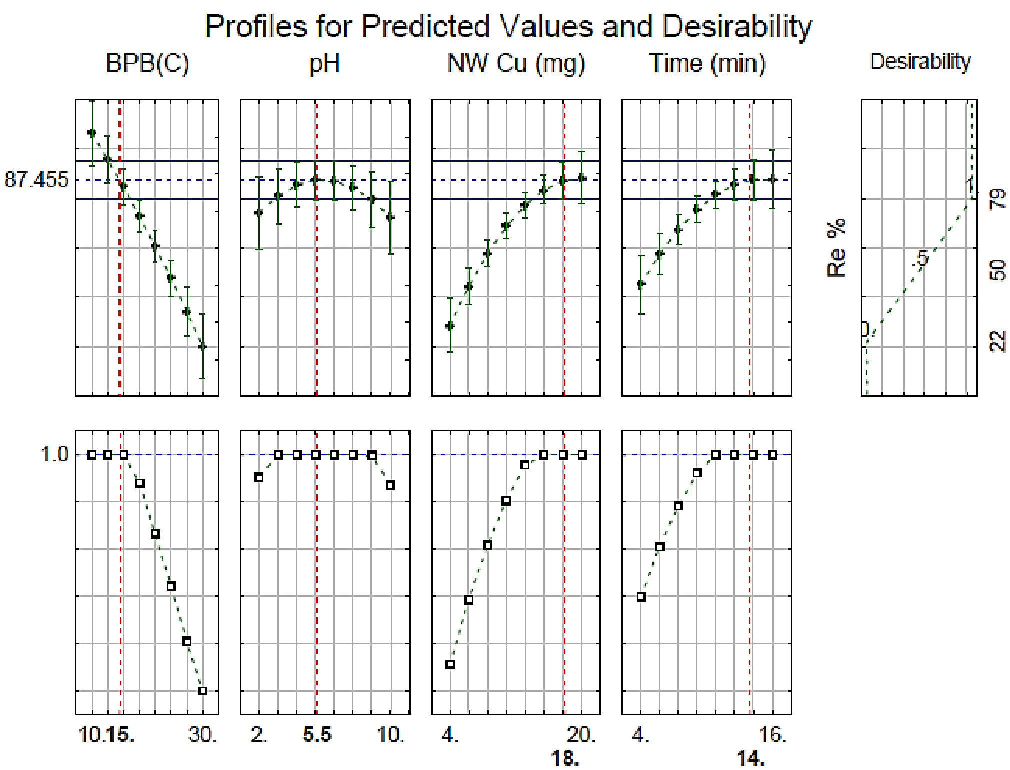

Fig.4. The obtained optimum values based on DF

3.4. Adsorption isotherm models

To assess the adsorption mechanism and achieve maximum adsorption capacity (q_m), various isotherms models like Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (DR) were investigated (Table 3). According to the results of different models, Langmuir was more suitable than others which were due to its higher R^2 (0.9905). The Langmuir model explains that the adsorption of dyes onto adsorbent is monolayer and on the homogeneous surface of the adsorbent. The calculated q_m, according to the Langmuir model, was 123.45 mg g^{-1}. In the Freundlich model, the n values of more than 1 proved the favourable adsorption condition. In the Dubinin-Radushkevich model, the values of mean energy (E) less than 8 kJ mol^{-1} represented that the adsorption process of BPB dye was probably controlled physically.

3.5. Kinetic models

In the evaluation adsorption process, the adsorption kinetics can be considered an essential characteristic. To this end, pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion kinetic models were used to discuss the adsorption behaviour (Table 4). Results proved that the adsorption of BPB by Cu-NW-AC was followed by pseudo-second-order which was due to its high R^2 (0.993).

Recently, many techniques based on nanoadsorbents have been used for the removal of dye and other organic material (BTEX) in water samples [24-31]. To further demonstrate the superiority of our proposed method, a comparison of the important features of the proposed method with those reported in the literature [32-35] is given in Table 5.

Table 3. Different isotherm models for removal of BPB by Cu-NW-AC.

Isotherm models	**Equation**	**Factors**	**Adsorbent (g)**	**Time (min)**
			0.018	**14**
Langmuir	$C_e/q_e = 1/(K_aQ_m) + C_e/Q_m$	$q_m(mgg^{-1})$	123.45	
		$k_a(1\ mg^{-1})$	3.681	
		R^2	0.9905	
Freundlich	$Ln\ q_e = \ln K_F + (1/n) \ln C_e$	$\frac{1}{n}$	0.295	
		$K_f(lmg^{-1})$	83.21	
		R^2	0.2245	
Temkin	$q_e = B_l \ln K_T + B_l \ln C_e$	β_1		
		$K_T(1\ mg^{-1})$	100.37	
		R^2	0.1863	
Dubinin and Radushkevich	$Ln\ q_e = \ln Q_m - K\varepsilon^2$	β		
		q_s	100.8	
		R^2	0.4356	

Table 4. Different kinetic models for removal of BPB by Cu-NW-AC

Kinetic models	Equation	Factors	Adsorbent (g)	Concentration (mg L^{-1})
			0.018	15
Pseudo-first order	$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2/303}$	$k_1(min^{-1})$	0.224	
		$q_e(mgg^{-1})$	19.31	
		R^2	0.967	
Pseudo-second-order-kinetic	$t/q_t = 1/k_2 q_e^2 + (1/q_e)t$	$k_2(min^{-1})$	------	
		$q_e(mg\ g^{-1})$	-------	
		R^2	0.993	
Intraparticle diffusion	$q_e = k_3 t^{\frac{1}{2}} + c$	$k\left(mg\ g^{-1} min^{-\frac{1}{2}}\right)$	-------	
		$c(mg\ g^{-1})$	-------	
		R^2	0.997	
Elovich	$q_t = \ln\frac{(\alpha\beta)}{\beta} + \left(\frac{1}{\beta}\right)\ln t$	$\beta\ (g\ mg^{-1})$	-------	
		$\alpha\ (mg\ g^{-1} min^{-1})$	-------	
		R^2	0.987	

Table 5. Comparison of the proposed method with some adsorbent reported in the literature

Adsorbents	Sorptioncapacity (mg g^{-1})	pH	Contact times (min)	References
Fe_3O_4-CuO-AC	123.45	9	120	[32]
PAN@SiO_2	129.60	3	80	[33]
Hb/Fe_3O_4 composite	101	4	24 h	[34]
α-chitin nanoparticle	27.72		120	[35]
Cu-NW-AC	123.45	5.5	14	Thisstudy

4. Conclusion

The aim of the presented work was the fabrication and application of Cu-NW-AC as an adsorbent for the removal of BPB dye from water samples. After synthesis, the proposed adsorbent was characterized by TEM and BET analyses. To evaluate effective factors, and their interactions, and obtain valid optimum values, EDM-based RSM was used. Moreover, to judge the accuracy and adequacy of the applied model, ANOVA was incorporated. The adsorption kinetic models and equilibrium parameters, such as kinetic rate constants, the Langmuir, Freundlich, Temkin, D–R constants, and maximum capacity of adsorption, were obtained from the adsorption experiments. These parameters are very important for scale-up batch experiments. A comparison of kinetic models on the overall adsorption rate showed that the dye adsorbent system was best described by the pseudo-second-order rate model. The adsorption data fitted well with the Langmuir isotherm.

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